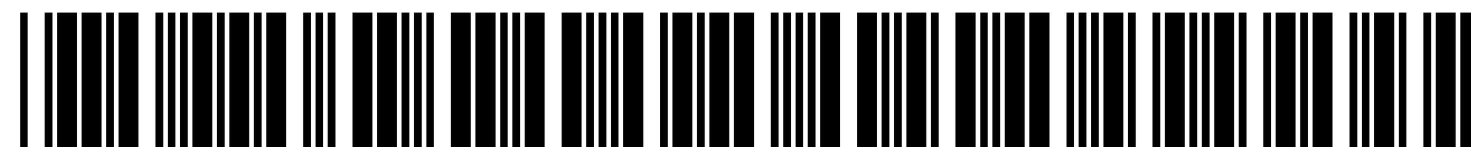

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(12) **United States Patent**
Byun

(10) **Patent No.: US 6,936,538 B2**
(45) **Date of Patent: Aug. 30, 2005**

(54) **METHOD AND APPARATUS FOR DEPOSITING TUNGSTEN AFTER SURFACE TREATMENT TO IMPROVE FILM CHARACTERISTICS**

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(73) Assignee: **Applied Materials, Inc.**, Santa Clara, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/196,514**

(22) Filed: **Jul. 15, 2002**

(65) **Prior Publication Data**

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Related U.S. Application Data

(60) Provisional application No. 60/305,765, filed on Jul. 16, 2001.

(51) **Int. Cl.**^{7} **H01L 21/44**
(52) **U.S. Cl.** **438/680**
(58) **Field of Search** 438/680

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Assistant Examiner—Fernando L. Toledo
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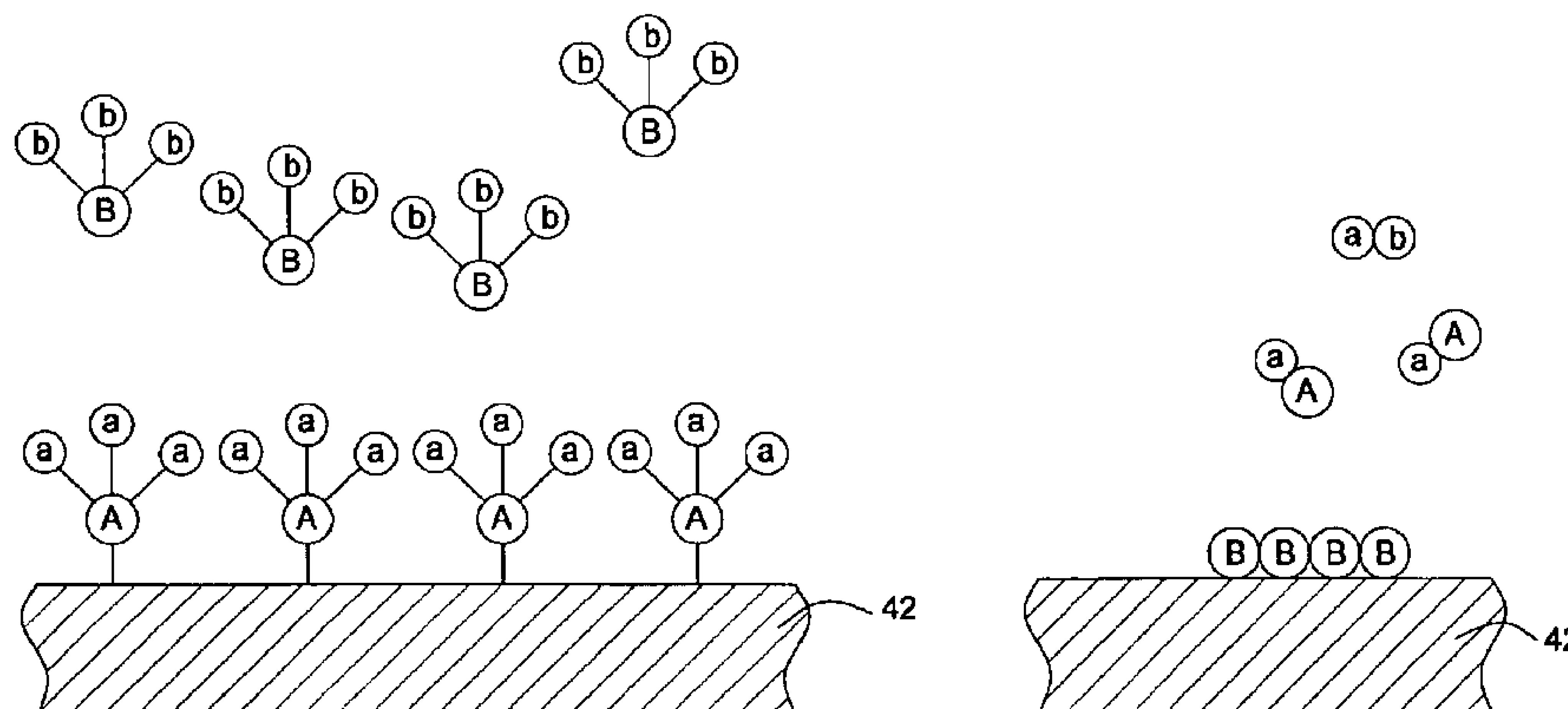
(57) **ABSTRACT**

A method and system to form a refractory metal layer over a substrate includes introduction of a reductant, such as PH_3 or B_2H_6, followed by introduction of a tungsten containing compound, such as WF_6, to form a tungsten layer. It is believed that the reductant reduces the fluorine content of the tungsten layer while improving the step coverage and resistivity of the tungsten layer. It is believed that the improved characteristics of the tungsten film are attributable to the chemical affinity between the reductants and the tungsten containing compound. The chemical affinity provides better surface mobility of the adsorbed chemical species and better reduction of WF_6 at the nucleation stage of the tungsten layer. The method can further include sequentially introducing a reductant, such as PH_3 or B_2H_6, and a tungsten containing compound to deposit a tungsten layer. The formed tungsten layer can be used as a nucleation layer followed by bulk deposition of a tungsten layer utilizing standard CVD techniques. Alternatively, the formed tungsten layer can be used to fill an aperture.

22 Claims, 10 Drawing Sheets



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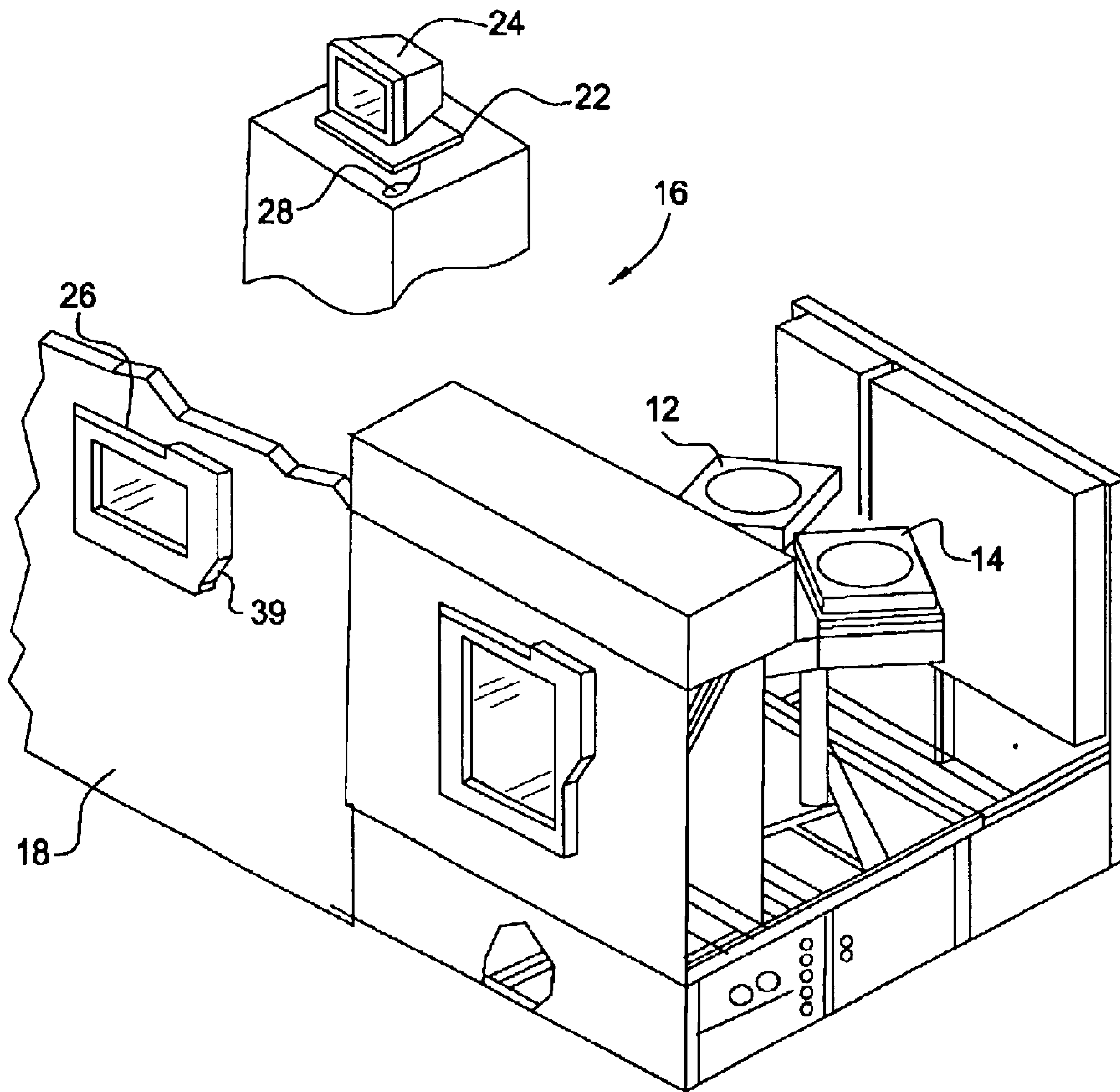

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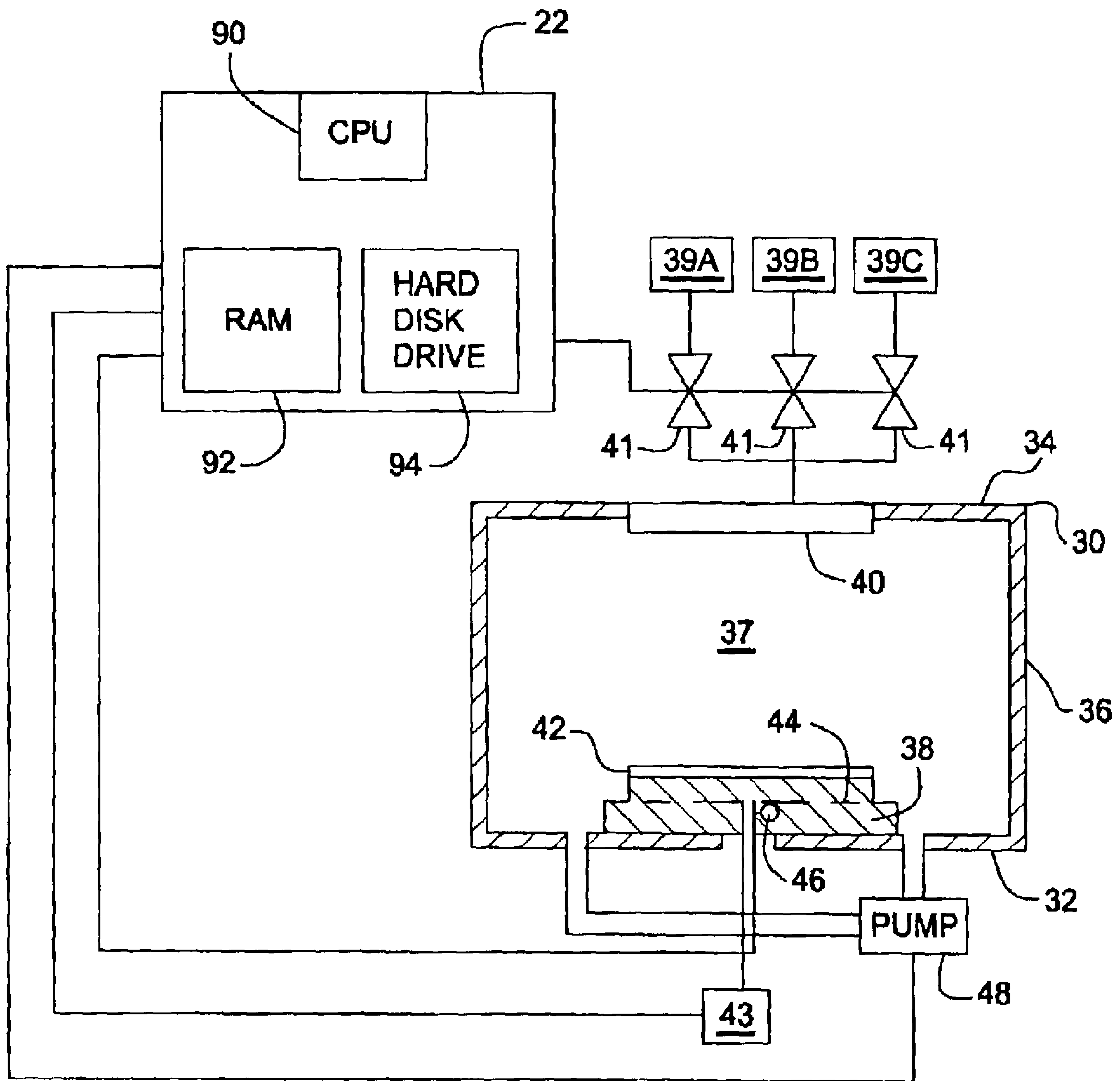
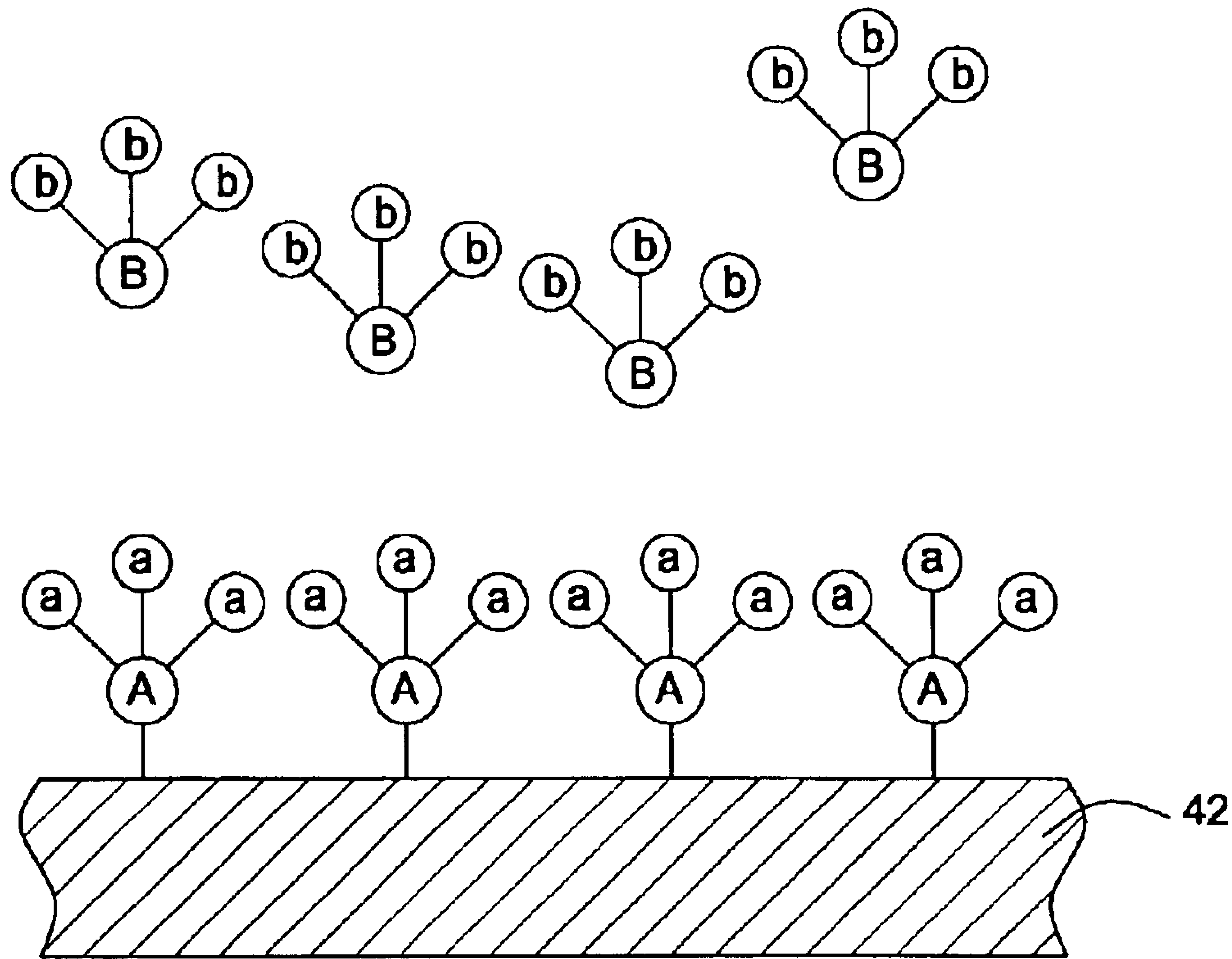


FIG. 2



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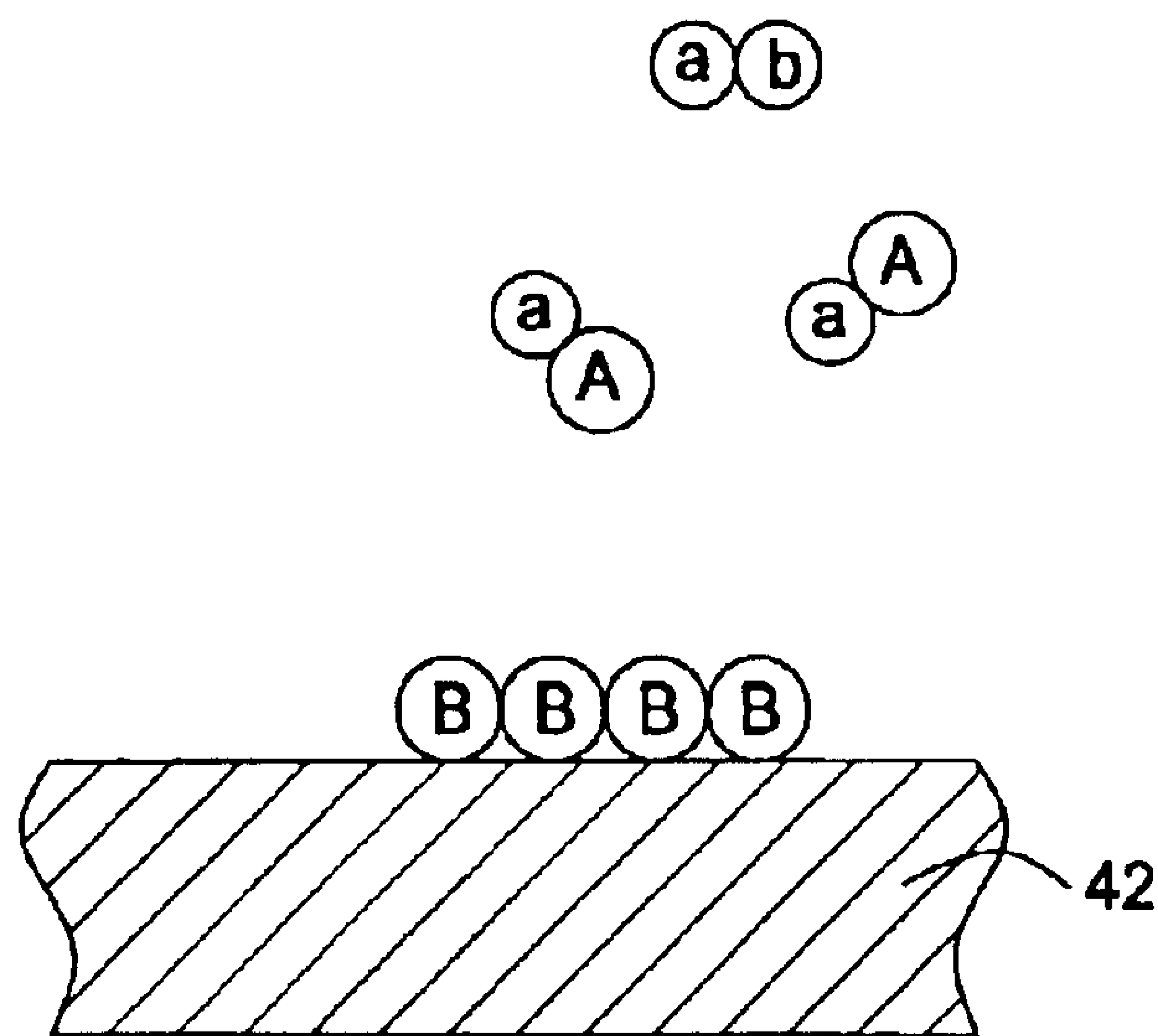


FIG. 4

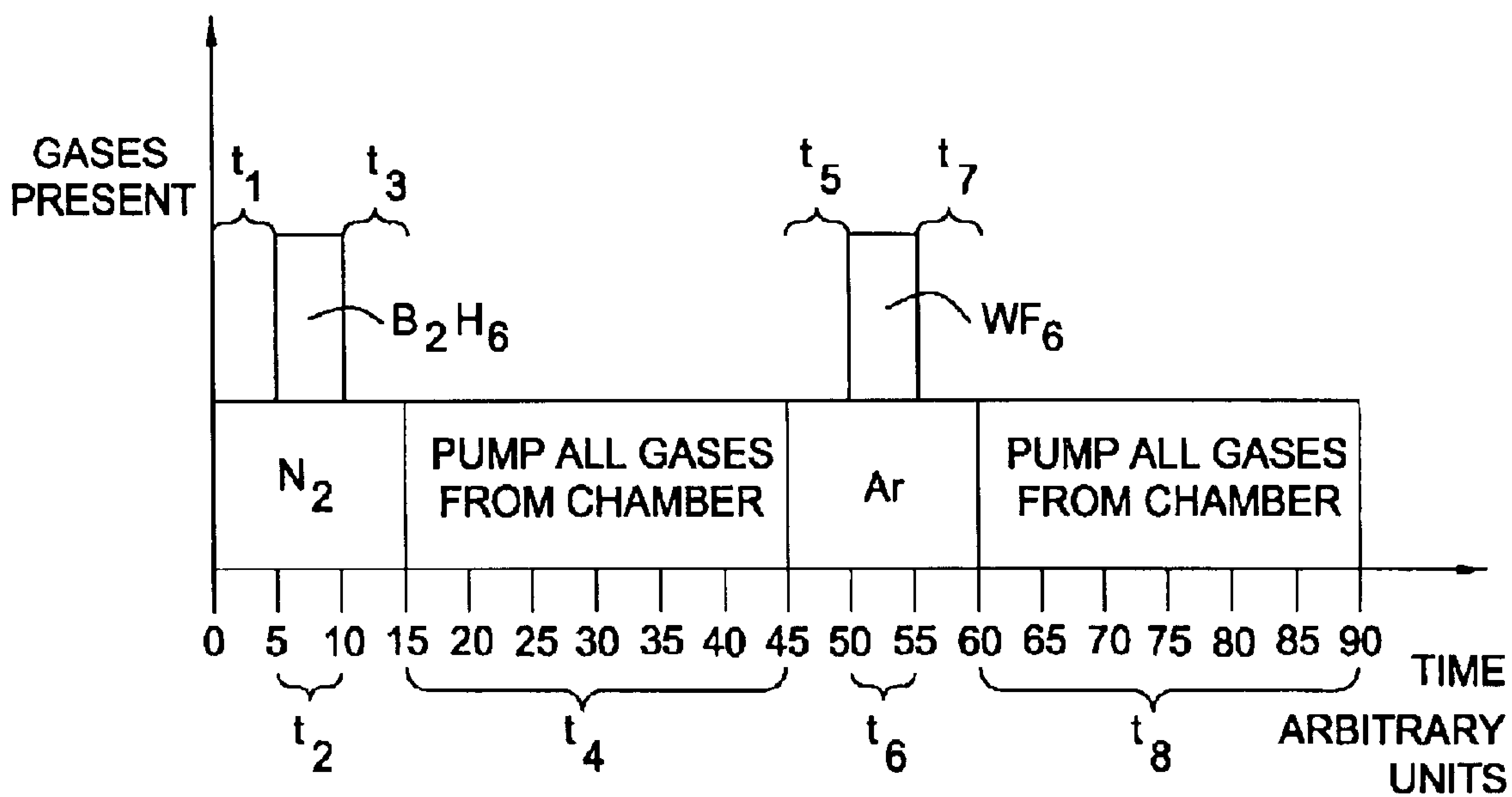
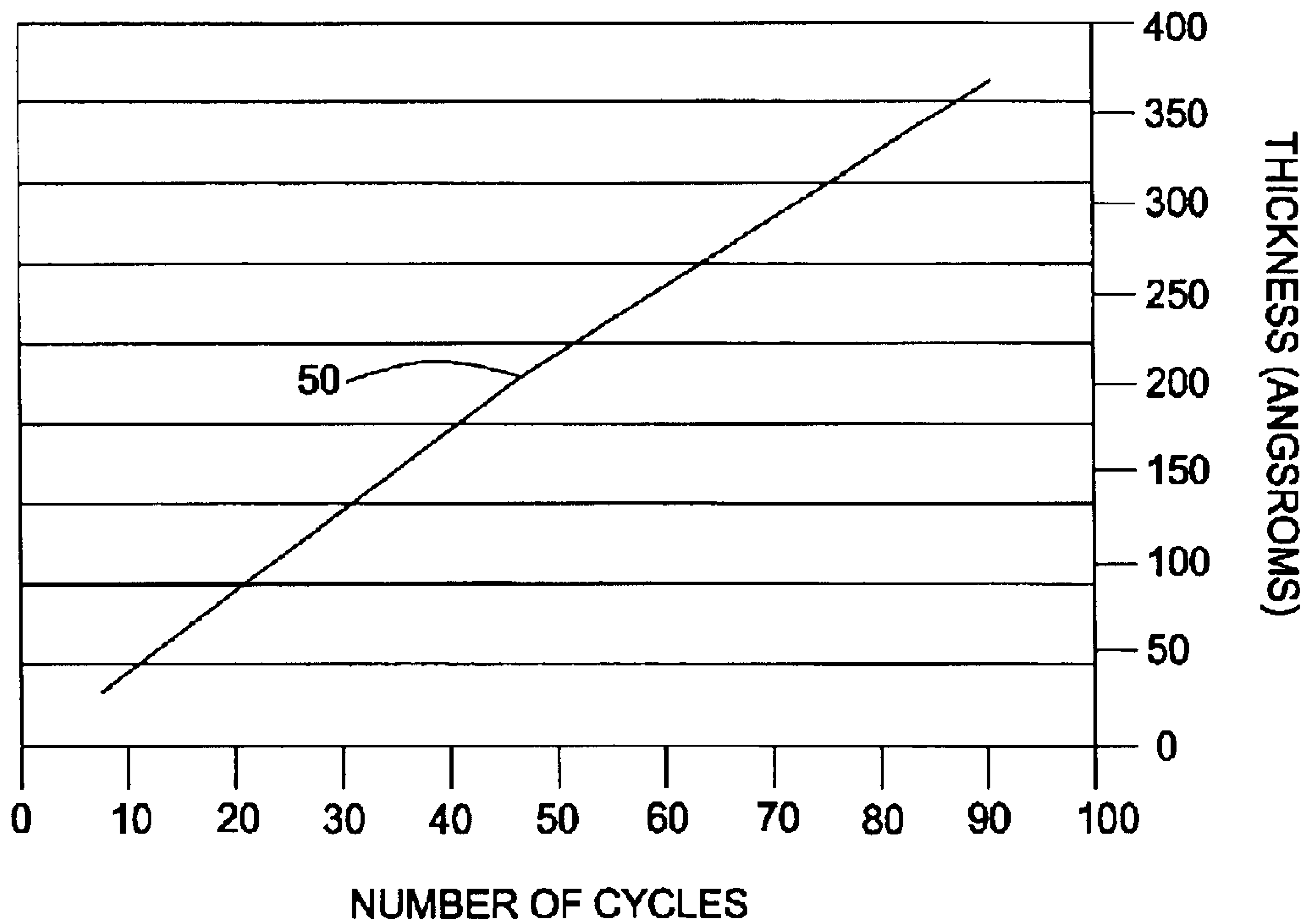


FIG. 5



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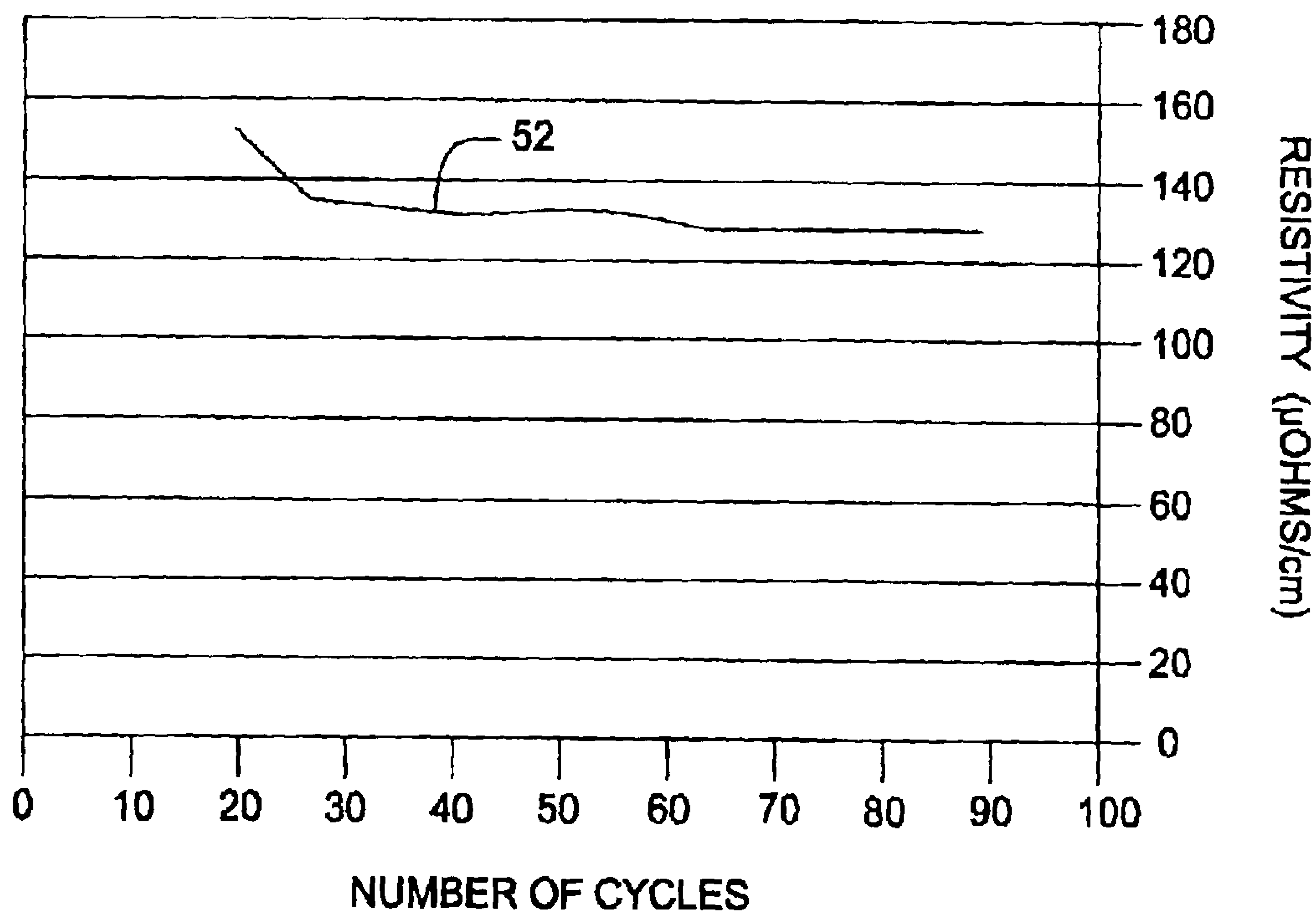

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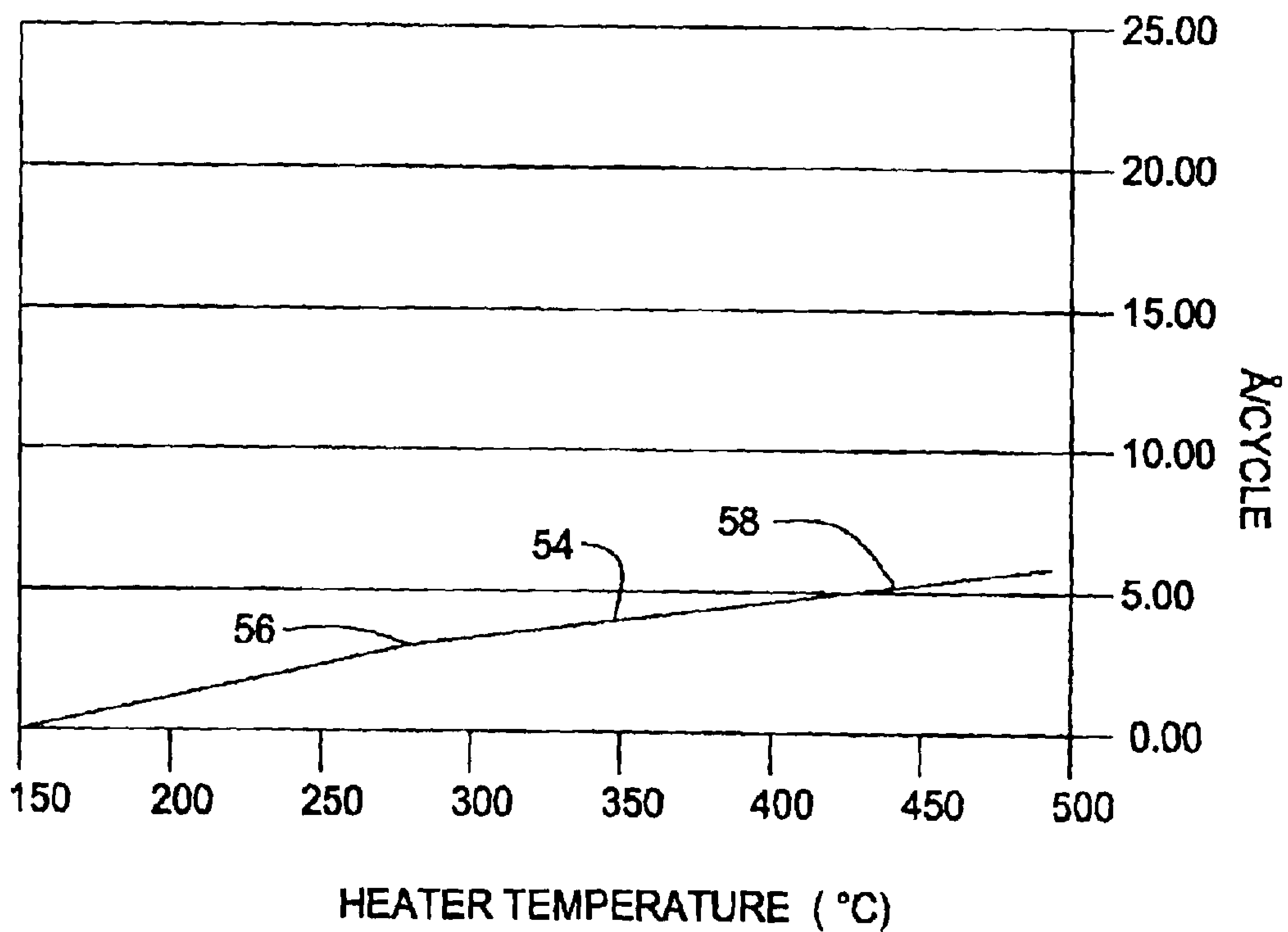

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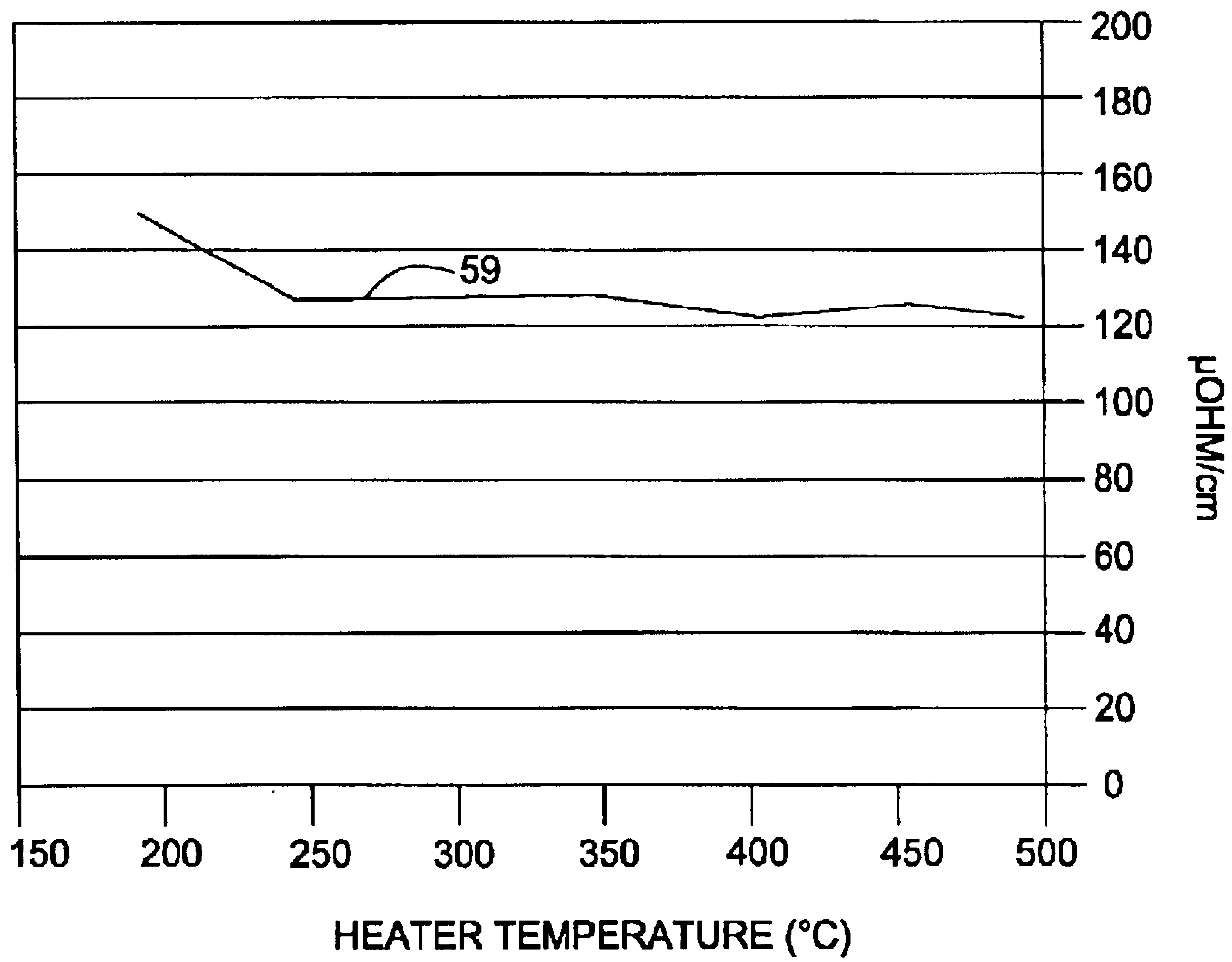

FIG. 9

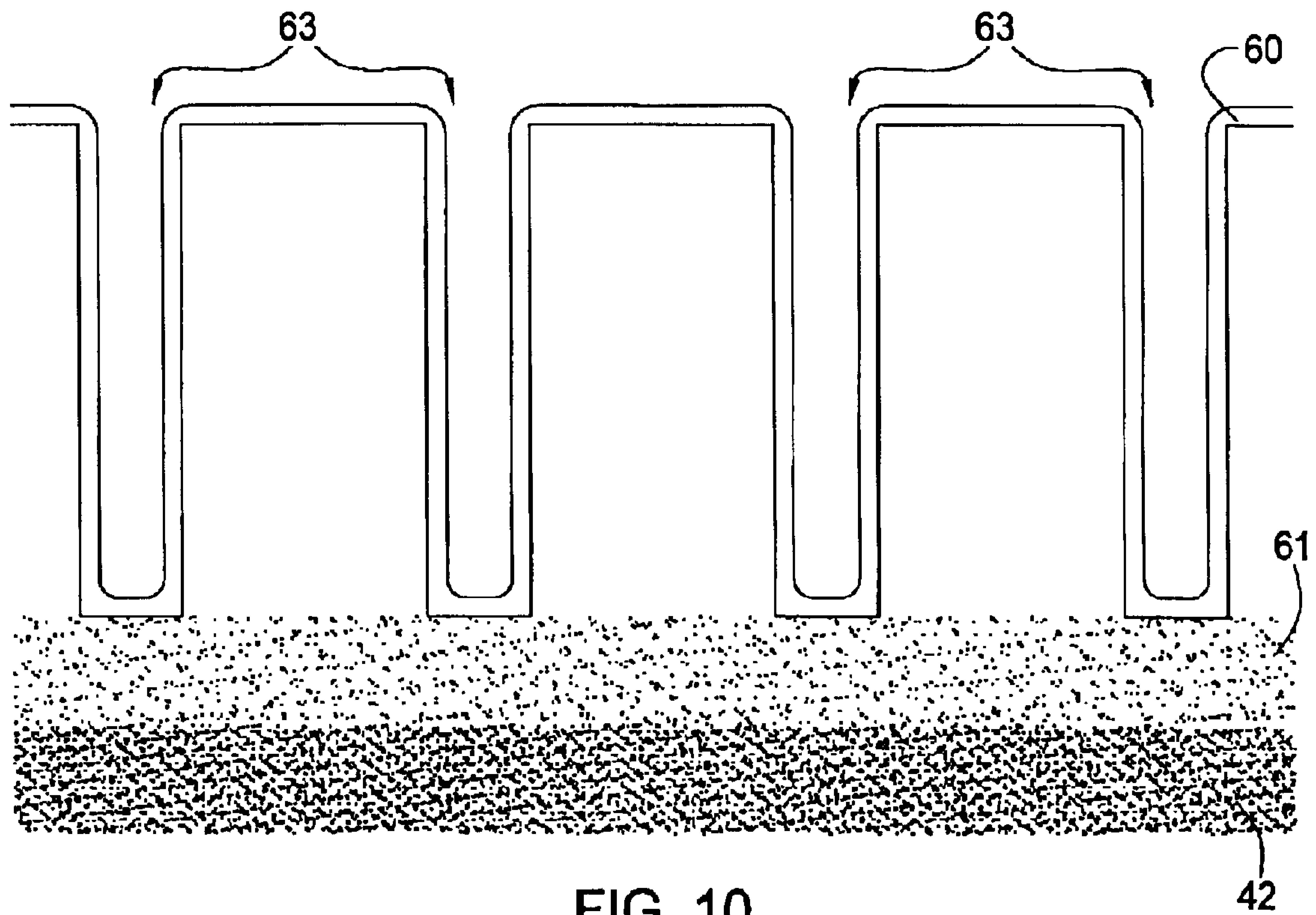

FIG. 10

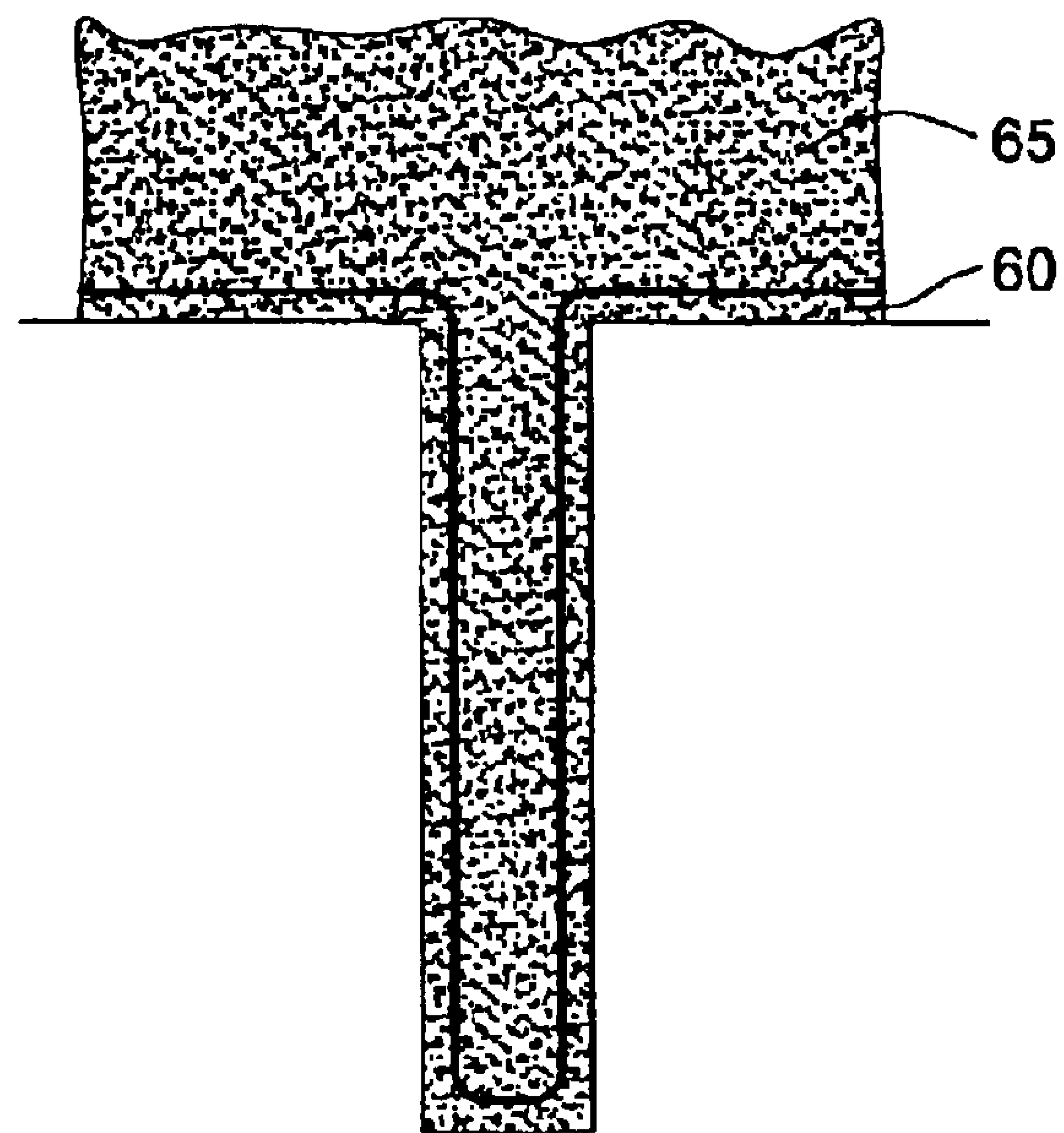

FIG. 11

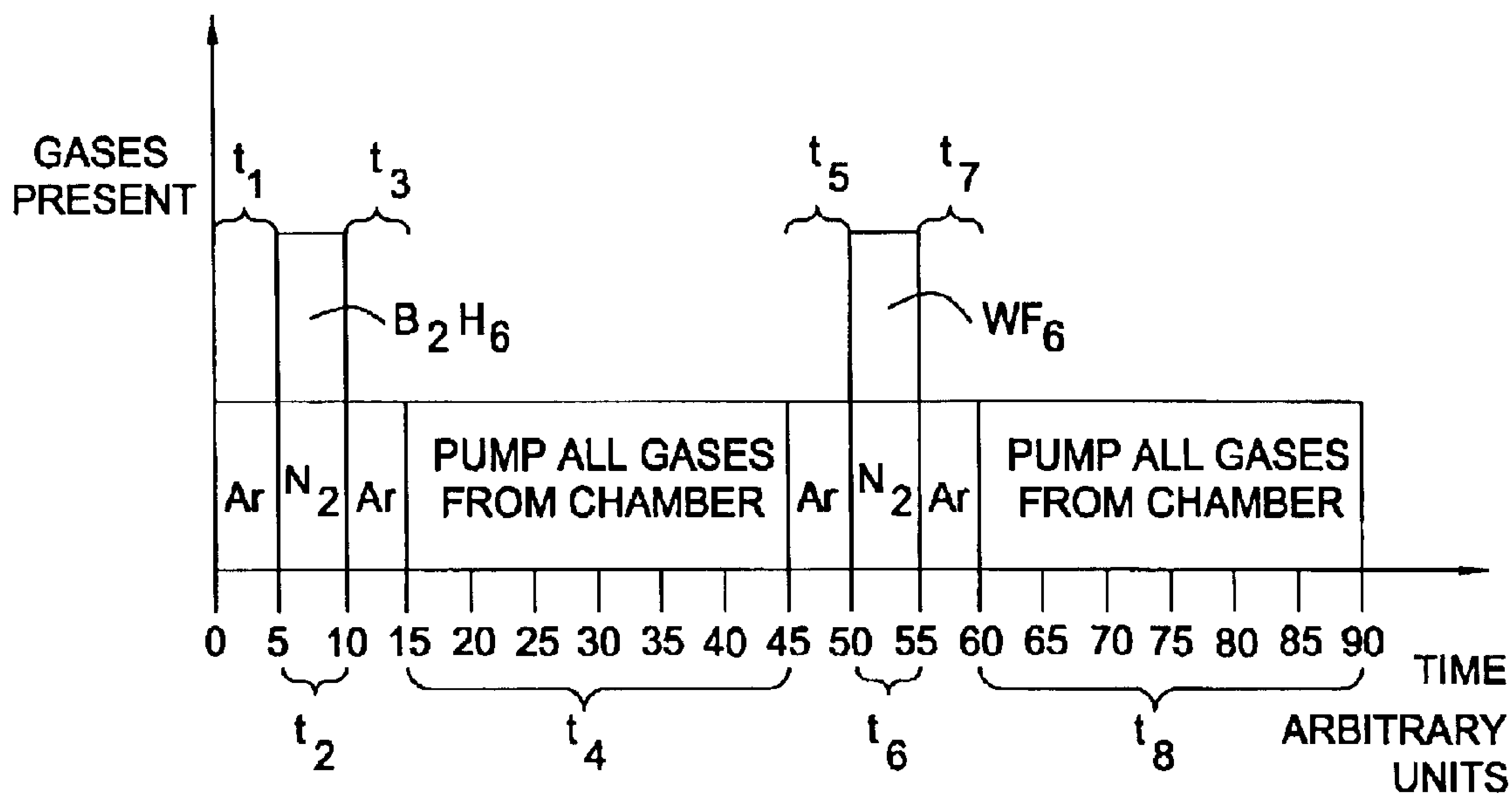

FIG. 12

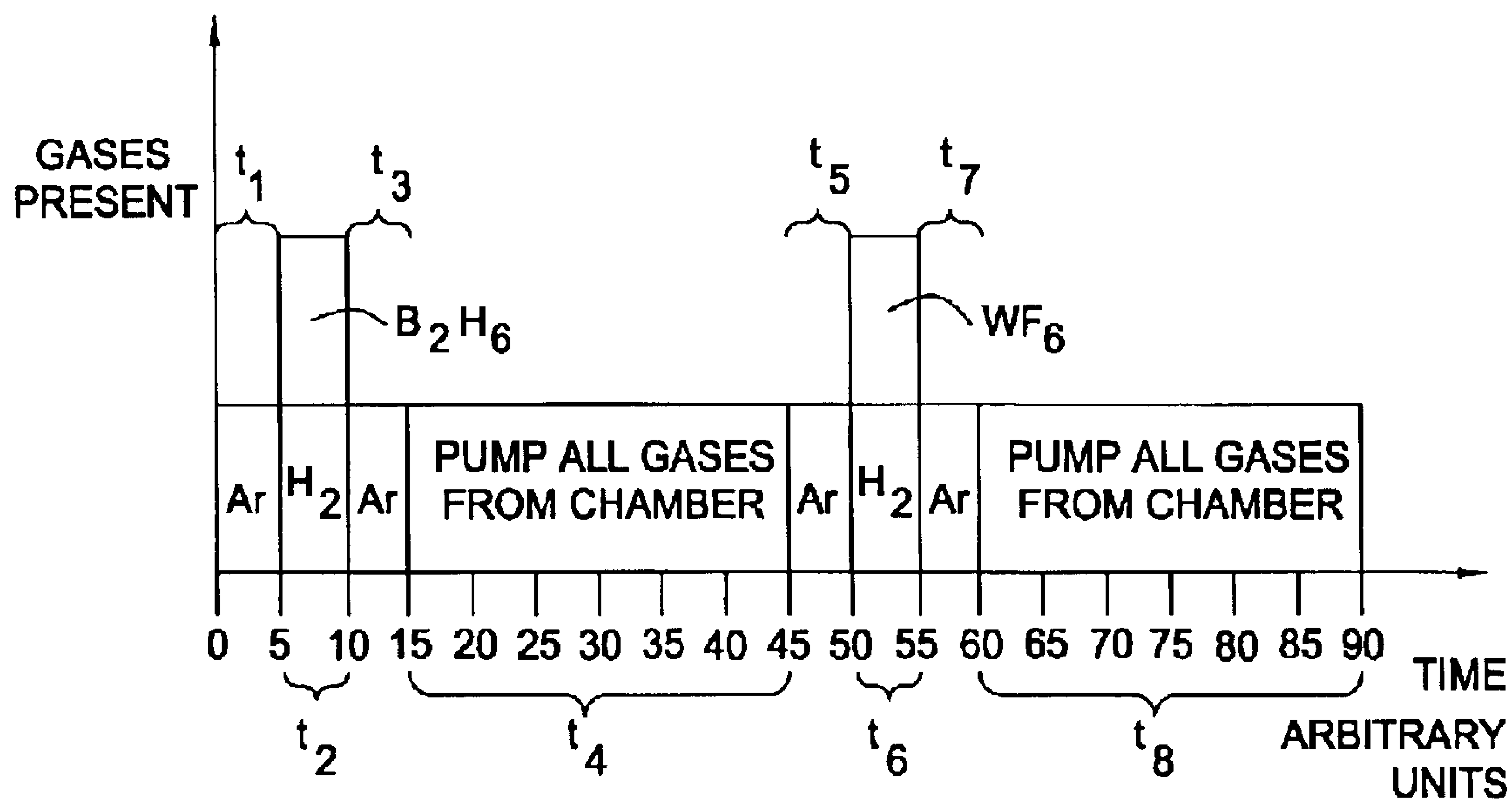

FIG. 13

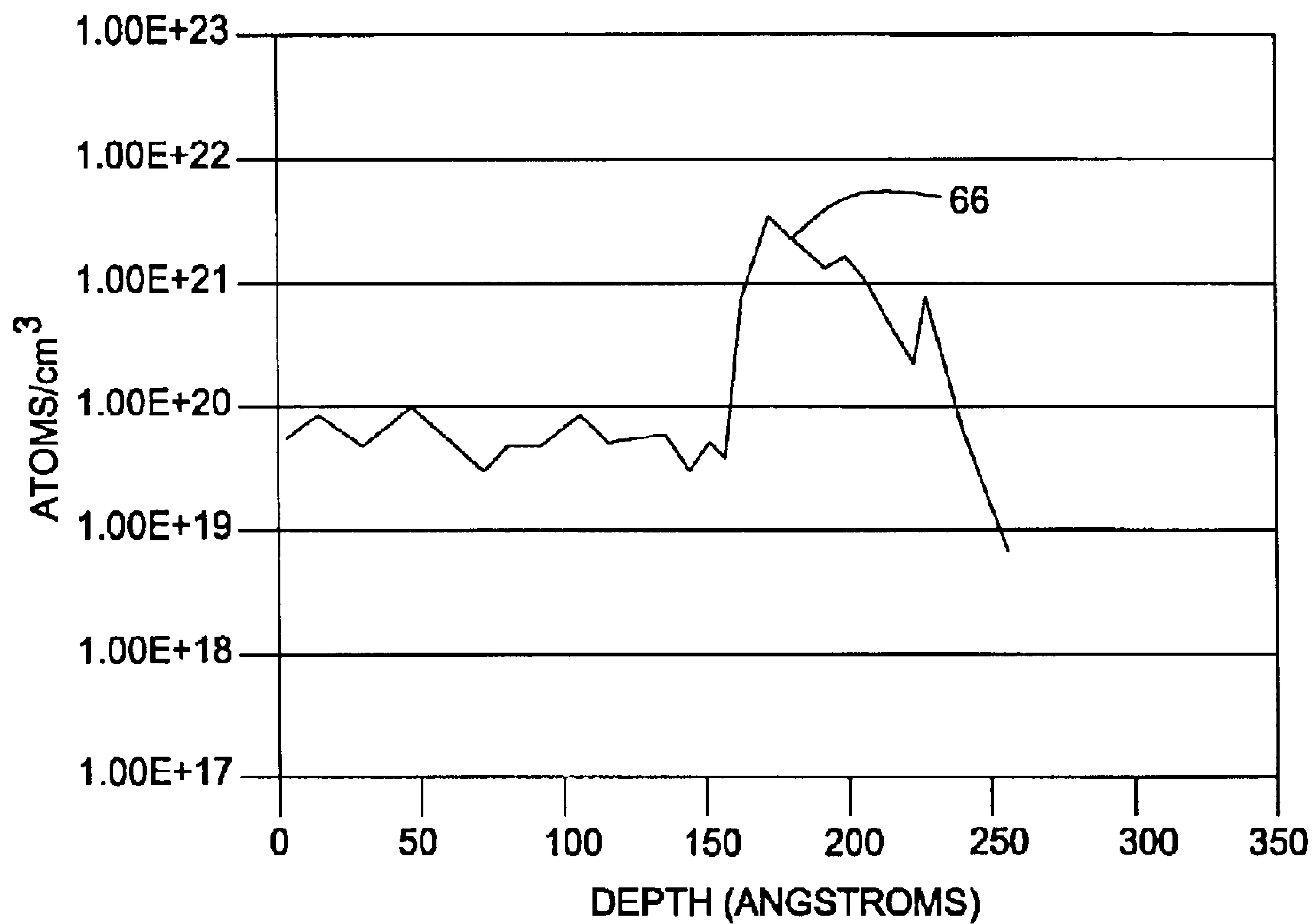

FIG. 14

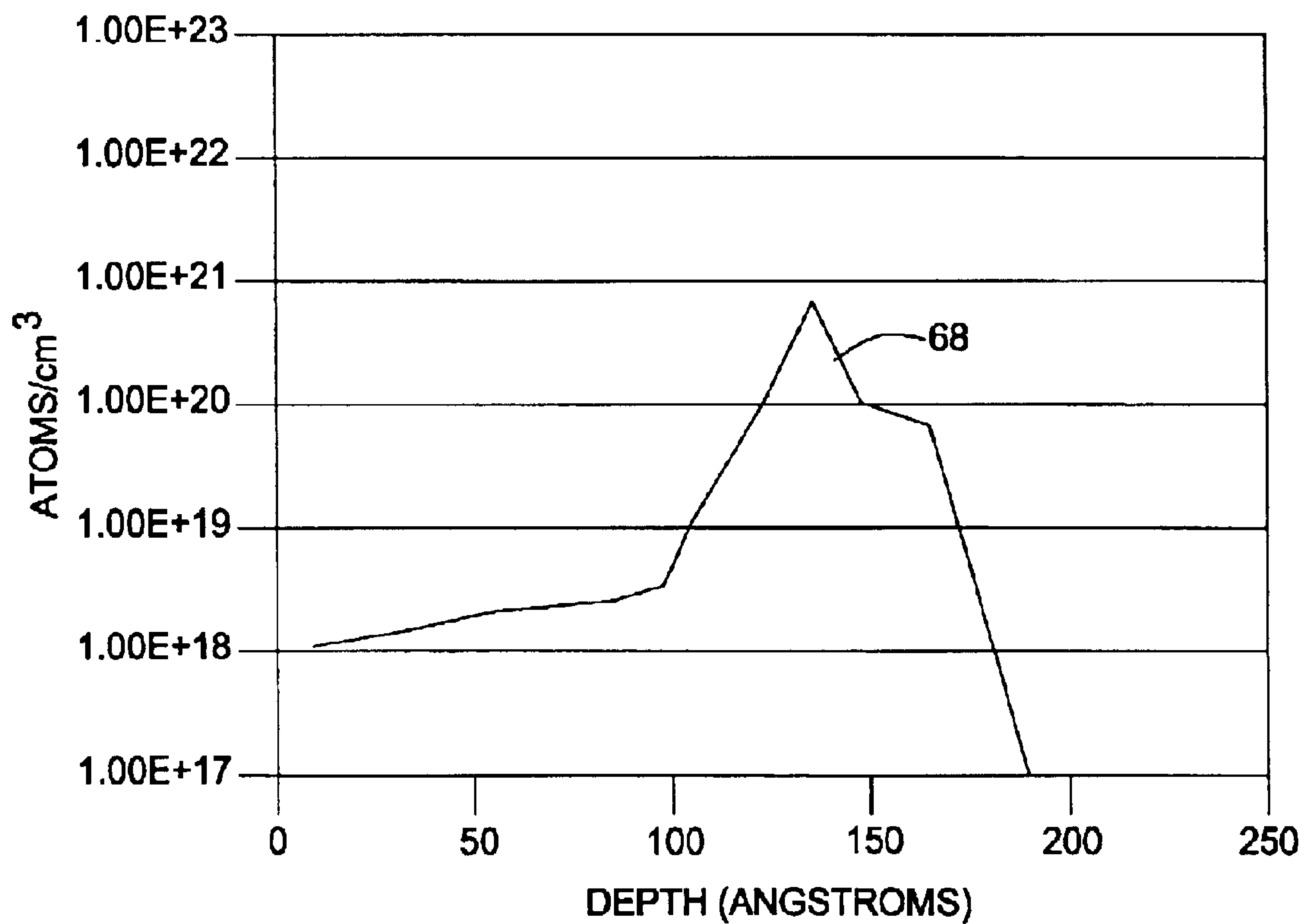

FIG. 15

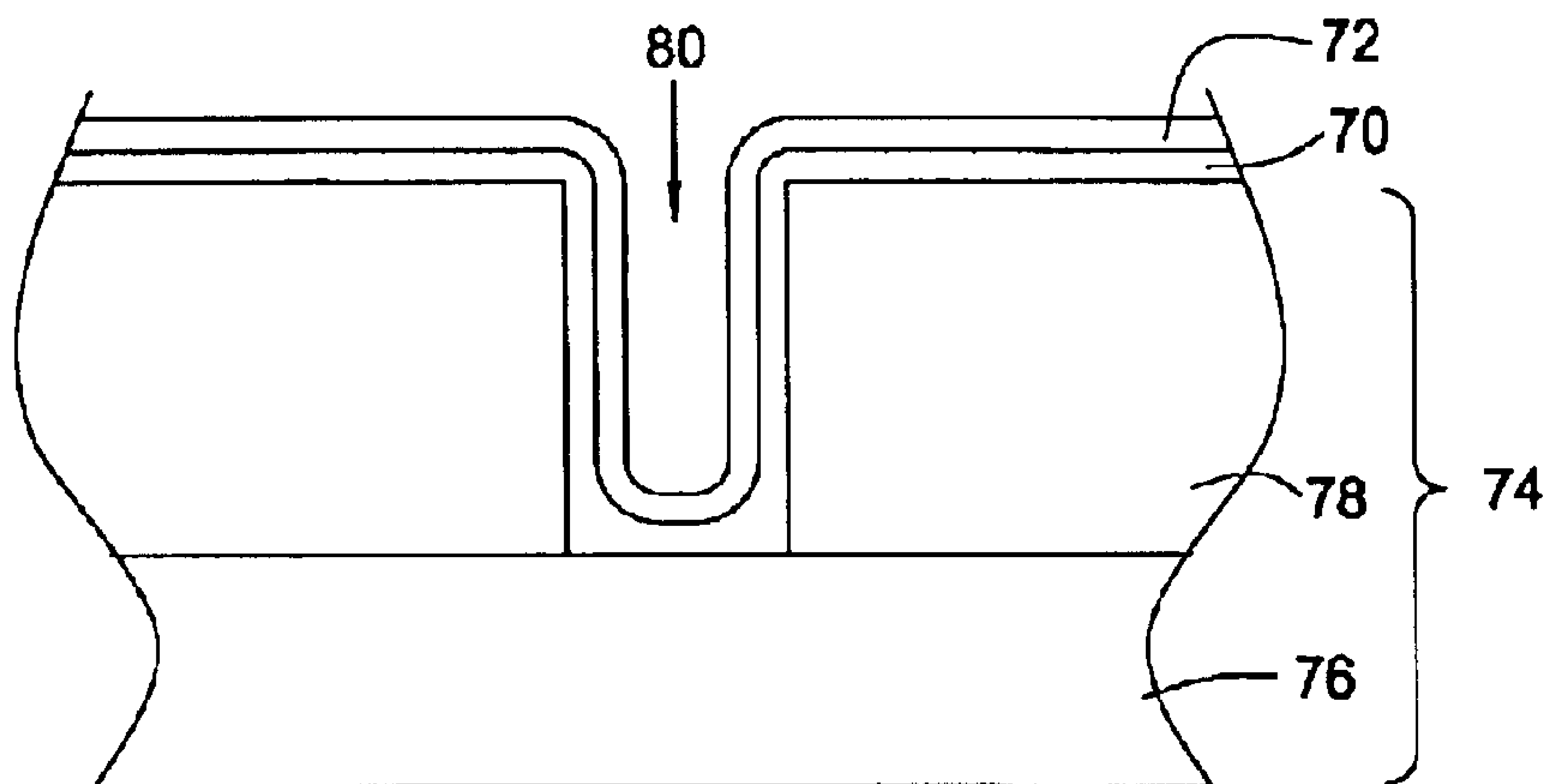

FIG. 16

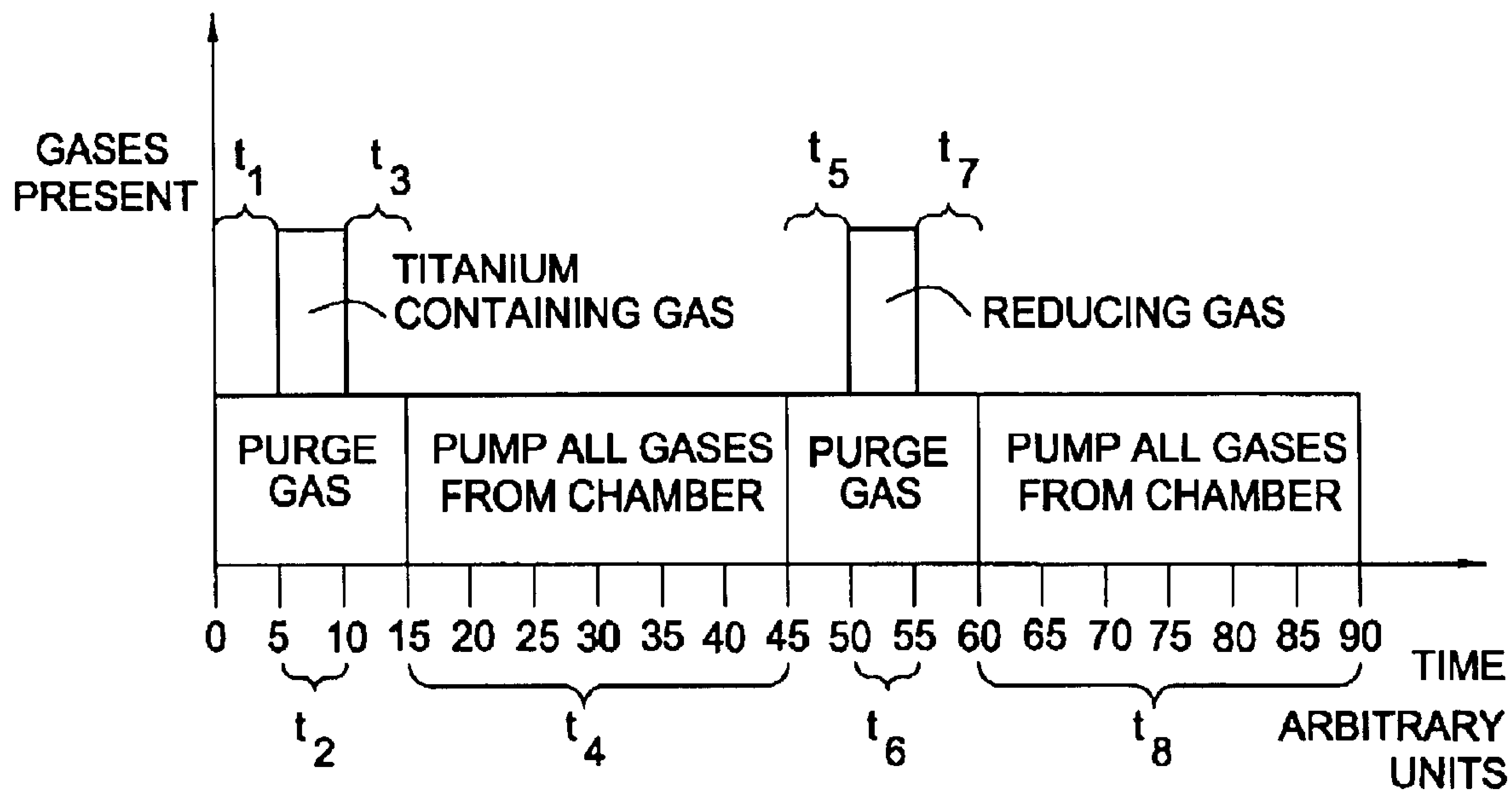

FIG. 17

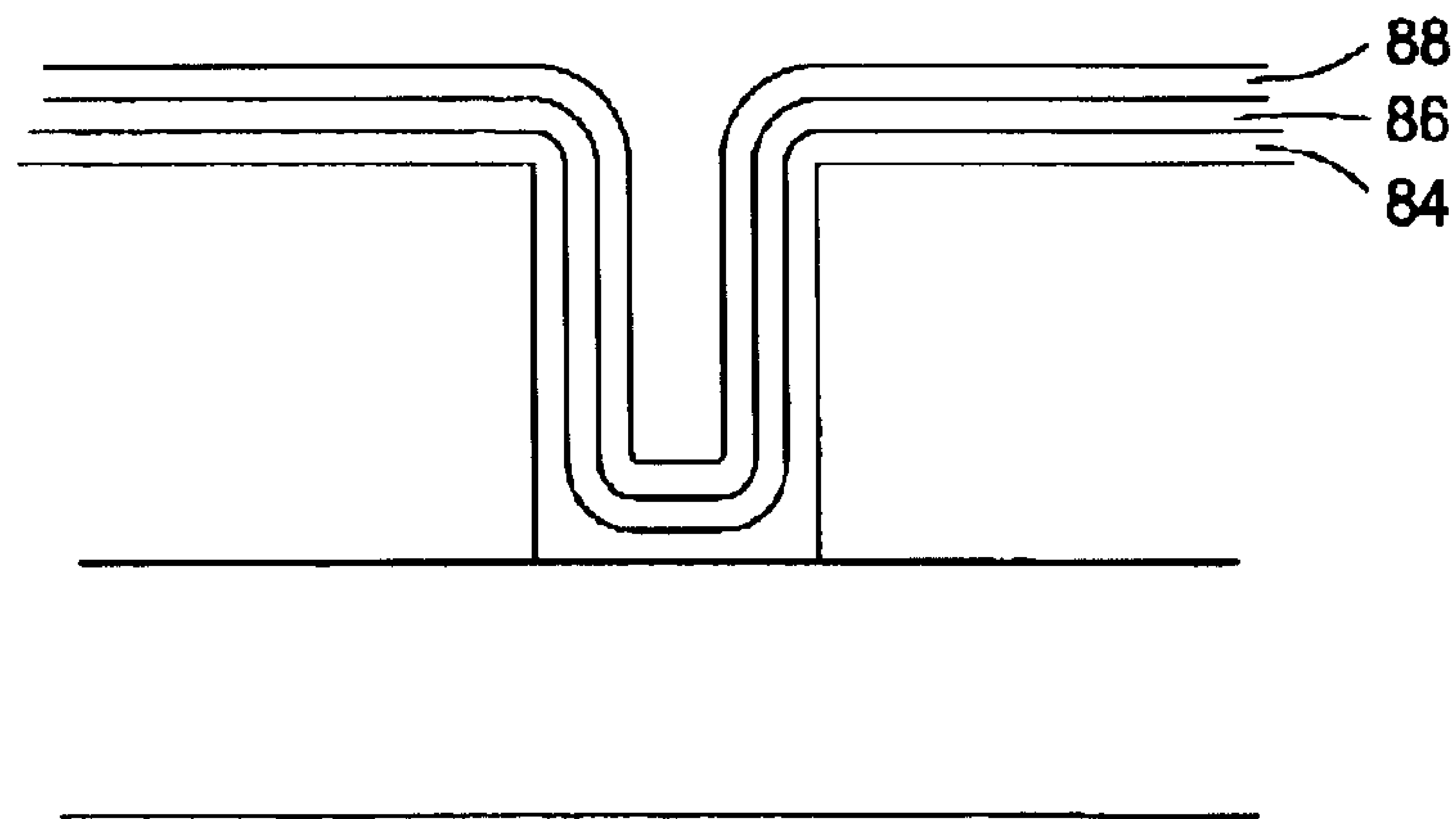

FIG. 18

METHOD AND APPARATUS FOR DEPOSITING TUNGSTEN AFTER SURFACE TREATMENT TO IMPROVE FILM CHARACTERISTICS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of U.S. Provisional Patent Application Ser. No. 60/305,765, filed Jul. 16, 2001, which is herein incorporated by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

Embodiments of the invention relate to the processing of semiconductor substrates. More particularly, embodiments of the invention relate to improvements in the process of depositing refractory metal layers on semiconductor substrates.

2. Description of the Related Art

The semiconductor processing industry continues to strive for larger production yields while increasing the uniformity of layers deposited on substrates having larger surface areas. These same factors in combination with new materials also provide higher density of circuits per unit area of the substrate. As circuit density increases, the need for greater uniformity and process control regarding layer thickness rises. As a result, various technologies have been developed to deposit layers on substrates in a cost-effective manner, while maintaining control over the characteristics of the layer. Chemical Vapor Deposition (CVD) is one of the most common deposition processes employed for depositing layers on a substrate. CVD is a flux-dependent deposition technique that requires precise control of the substrate temperature and precursors introduced into the processing chamber in order to produce a desired layer of uniform thickness. These requirements become more critical as substrate size increases (e.g., from 200 mm diameter substrates to 300 mm substrates), creating a need for more complexity in chamber design and gas flow technique to maintain adequate uniformity.

A variant of CVD that demonstrates superior step coverage compared to CVD, is Atomic Layer Deposition (ALD). ALD is based upon Atomic Layer Epitaxy (ALE) that was employed originally to fabricate electroluminescent displays. ALD employs chemisorption to deposit a saturated monolayer of reactive precursor molecules on a substrate surface. This is achieved by alternatingly pulsing an appropriate reactive precursor into a deposition chamber. Each injection of a reactive precursor is separated by an inert gas purge to provide an adsorbed atomic layer to previously deposited layers to form a uniform layer on the substrate. The cycle is repeated to form the layer to a desired thickness. A drawback with ALD techniques is that the deposition rate is much lower than typical CVD techniques by at least one order of magnitude.

Formation of film layers at a high deposition rate while providing adequate step coverage are conflicting characteristics often necessitating sacrificing one to obtain the other. This conflict is true particularly when refractory metal layers are deposited to cover apertures or vias during formation of contacts that interconnect adjacent metallic layers separated by dielectric layers. Historically, CVD techniques have been employed to deposit conductive material such as refractory metals in order to inexpensively and quickly fill vias. Due to the increasing density of semiconductor circuitry, tungsten has been used based upon superior step coverage to fill these high aspect ratio structures. As a result, deposition of tungsten employing CVD techniques enjoys wide application in semiconductor processing due to the high throughput of the process and good step coverage.

Depositing tungsten by traditional CVD methods, however, is attendant with several disadvantages. For example, blanket deposition of a tungsten layer on a semiconductor wafer is time-consuming at temperatures below 400° C. The deposition rate of tungsten may be improved by increasing the deposition temperature between approximately 500° C. to 550° C.; however, temperatures in this higher range may compromise the structural and operational integrity of the underlying portions of the integrated circuit being formed. Use of tungsten has also complicated photolithography steps during the manufacturing process as it results in a relatively rough surface having a reflectivity of 20% or less than that of a silicon substrate. Finally, tungsten has, proven difficult to deposit uniformly. Variance in film thickness of greater than 1% has been shown, thereby causing poor control of the resistivity of the layer. Several prior attempts to overcome the aforementioned drawbacks have been attempted.

For example, in U.S. Pat. No. 5,028,565 to Chang et al., which is assigned to the assignee of the present invention, a method is disclosed to improve, inter alia, uniformity of tungsten layers by varying the deposition chemistry. The method includes, in pertinent part, formation of a nucleation layer over an intermediate barrier layer before depositing the tungsten layer via bulk deposition. The nucleation layer is formed from a gaseous mixture of tungsten hexafluoride, hydrogen, silane and argon. The nucleation layer is described as providing a layer of growth sites to promote uniform deposition of a tungsten layer thereon. The benefits provided by the nucleation layer are described as being dependent upon the barrier layer present. For example, were the barrier layer formed from titanium nitride, the tungsten layer's thickness uniformity is improved as much as 15%. Were the barrier layer formed from sputtered tungsten or sputtered titanium tungsten, the benefits provided by the nucleation layer are not as pronounced.

A need exists, therefore, to provide techniques to improve the characteristics of refractory metal layers deposited on semiconductor substrates.

SUMMARY OF THE INVENTION

A method and system to form a refractory metal layer over a substrate includes introduction of a reductant, such as PH_3 or B_2H_6, followed by introduction of a tungsten containing compound, such as WF_6, to form a tungsten layer. It is believed that the reductant reduces the fluorine content of the tungsten layer while improving the step coverage and resistivity of the tungsten layer. It is believed that the improved characteristics of the tungsten film are attributable to the chemical affinity between the reductants and the tungsten containing compound. The chemical affinity provides better surface mobility of the adsorbed chemical species and better reduction of WF_6 at the nucleation stage of the tungsten layer.

The method can further include sequentially introducing a reductant, such as PH_3 or B_2H_6, and a tungsten containing compound to deposit a tungsten layer. The formed tungsten layer can be used as a nucleation layer followed by bulk deposition of a tungsten layer utilizing standard CVD techniques. Alternatively, the formed tungsten layer can be used to fill an aperture.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a perspective view of one embodiment of a semiconductor processing system in accordance with the present invention

FIG. **2** is a schematic cross-sectional view of one embodiment of the processing chambers shown above in FIG. **1**.

FIG. **3** is a schematic cross-sectional view of a substrate showing one possible mechanism of adsorption of a reductant over a substrate during sequential deposition.

FIG. **4** is a schematic cross-sectional view of a substrate showing one possible mechanism of adsorption of a refractory metal containing compound over the substrate after introduction of the reductant.

FIG. **5** is a graphical representation showing the concentration of gases present in a processing chamber, such as processing chamber as shown above in FIG. **2**.

FIG. **6** is a graphical representation showing the relationship between the number of ALD cycles and the thickness of a layer formed on a substrate employing sequential deposition techniques, in accordance with the present invention.

FIG. **7** is a graphical representation showing the relationship between the number of sequential deposition cycles and the resistivity of a layer formed on a substrate employing sequential deposition techniques, in accordance with the present invention.

FIG. **8** is a graphical representation showing the relationship between the deposition rate of a layer formed on a substrate employing sequential deposition techniques and the temperature of the substrate.

FIG. **9** is a graphical representation showing the relationship between the resistivity of a layer formed on a substrate employing sequential deposition techniques and the temperature of the substrate, in accordance with the present invention.

FIG. **10** is a schematic cross-sectional view of one embodiment of a patterned substrate having a nucleation layer formed thereon employing sequential deposition techniques, in accordance with the present invention.

FIG. **11** is a schematic cross-sectional view of one embodiment of the substrate, shown above in FIG. **10**, with a refractory metal layer formed atop of the nucleation layer employing CVD, in accordance with the present invention.

FIG. **12** is a graphical representation showing the concentration of gases present in a processing chamber, such as the processing chamber as shown above in FIG. **2**, in accordance with an alternative embodiment of the present invention.

FIG. **13** is a graphical representation showing the concentration of gases present in a processing chamber, such as processing chamber as shown above in FIG. **2**, in accordance with an alternative embodiment of the present invention.

FIG. **14** is a graphical representation showing the fluorine content versus depth of a refractory metal layer formed on a substrate employing ALD, either Ar or N_2 being a carrier gas.

FIG. **15** is a graphical representation showing the fluorine content versus depth of a refractory metal layer formed on a substrate employing ALD with H_2 being a carrier gas.

FIG. **16** is a schematic cross-sectional view of one embodiment of a substrate shown above in FIGS. **3** and **4** upon which a layer of either PH_3 or B_2H_6 is disposed between a substrate and a tungsten layer, in accordance with one embodiment of the present invention.

FIG. **17** is a graphical representation showing the concentration of gases present in a processing chamber, such as processing chamber as shown above in FIG. **2**, in accordance with one embodiment of the present invention.

FIG. **18** is a schematic cross-sectional view of one embodiment of a substrate shown above in FIGS. **3** and **4** in which a titanium-containing layer is deposited between a substrate and a layer of either PH_3 or B_2H_6, in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIG. **1**, an exemplary wafer processing system includes one or more processing chambers **12** and **14** disposed in a common work area **16** surrounded by a wall **18**. Processing chambers **12** and **14** are in data communication with a controller **22** that is connected to one or more monitors, shown as **24** and **26**. The monitors typically display common information concerning the process associated with processing chambers **12** and **14**. One of the monitors **26** is mounted on wall **18**, with the remaining monitor **24** being disposed in work area **16**. Operational control of processing chambers **12** and **14** may be achieved by the use of a light pen, associated with one of the monitors **24** and **26**, to communicate with controller **22**. For example, light pen **28** is associated with monitor **24** and facilitates communication with controller **22** through monitor **24**. Light pen **39** facilitates communication with controller **22** through monitor **26**.

Referring both to FIGS. **1** and **2**, each of processing chambers **12** and **14** includes a housing **30** having a base wall **32**, a cover **34** disposed opposite to base wall **32**, and a sidewall **36** extending therebetween. Housing **30** defines a chamber **37**, and a pedestal **38** is disposed within processing chamber **37** to support a substrate **42**, such as a semiconductor wafer. Pedestal **38** may be mounted to move between cover **34** and base wall **32**, using a displacement mechanism (not shown), but the position thereof is typically fixed. Supplies of processing gases **39***a*, **39***b* and **39***c* are in fluid communication with processing chamber **37** via a showerhead **40**. Regulation of the flow of gases from supplies **39***a*, **39***b* and **39***c* is effectuated via flow valves **41**.

Depending on the specific process, substrate **42** may be heated to a desired temperature prior to layer deposition via a heater embedded within pedestal **38**. For example, pedestal **38** may be resistively heated by applying an electric current from AC power supply **43** to heater element **44**. Substrate **42** is, in turn, heated by pedestal **38**, and can be maintained within a desired process temperature range of, for example, about 20° C. to about 750° C. A temperature sensor **46**, such as a thermocouple, is also embedded in wafer support pedestal **38** to monitor the temperature of pedestal **38** in a conventional manner. For example, the measured temperature may be used in a feedback loop to control the electrical current applied to heater element **44** by power supply **43** such that the substrate temperature can be maintained or controlled at a desired temperature that is suitable for the particular process application. Optionally, pedestal **38** may be heated using radiant heat (not shown). A vacuum pump **48** is used to evacuate processing chamber **37** and to help maintain the proper gas flows and pressure inside processing chamber **37**.

Referring to FIGS. **1** and **2**, one or both of processing chambers **12** and **14**, discussed above may operate to deposit refractory metal layers on the substrate employing sequential deposition techniques. One example of sequential depo-

sition techniques in accordance with the present invention includes atomic layer deposition (ALD). The term "substrate" as used herein includes the substrate, such as semiconductor substrates and glass substrates, as well as layers formed thereover, such as dielectric layers (i.e., SiO_2) and barrier layers (i.e., titanium, titanium nitride and the like).

Not wishing to be bound by theory, FIG. **3** is a schematic cross-sectional view of a substrate showing one possible mechanism of adsorption of a reductant over a substrate during sequential deposition. The terms "adsorption" or "adsorb" as used herein are defined to include chemisorption, physisorption, or any attractive and/or bonding forces which may be at work and/or which may contribute to the bonding, reaction, adherence, or occupation of a portion of an exposed surface of a substrate structure. During the sequential deposition technique, in accordance with the present invention, a batch of a first processing gas, in this case "Aa_x," results in a layer of "A" being deposited on substrate **42** having a surface of ligand "a" exposed to processing chamber **37**. Layer "A" may be a monolayer, more than a monolayer, or less than a monolayer. Thereafter, a purge gas enters processing chamber **37** to purge gas "Aa_x," which has not been incorporated into the layer of A. FIG. **4** is a schematic cross-sectional view of a substrate showing one possible mechanism of adsorption of a refractory metal containing compound over the substrate after introduction of the reductant. After purging gas "Aa_x" from processing chamber **37**, a second batch of processing gas, "Bb_y," is introduced into processing chamber **37**. The "a" ligand present on the substrate surface reacts with the "b" ligand and "B" atom, releasing molecules, for example, "ab" and "aA," which move away from substrate **42** and are subsequently pumped from processing chamber **37**. In this manner, a surface comprising a layer of B compound remains upon substrate **42** and exposed to processing chamber **37**, shown in FIG. **4**. The composition of the layer of B compound may be a monolayer or less of atoms typically formed employing ALD techniques. In other embodiments, more than a monolayer of B compound may be formed during each cycle. Alternatively, the layer of compound B may include a layer of multiple atoms (i.e. other atoms besides atoms of B). In such a case, the first batch and/or the second batch of processing gases may include a mixture of process gases, each of which has atoms that would adhere to substrate **42**. The process proceeds cycle after cycle, until the desired thickness is achieved.

Referring to both FIGS. **3** and **4**, although any type of processing gas may be employed, in the present example, the reductant "Aa_x" may comprise B_2H_6 or PH_3 and the refractory metal containing compound, Bb_y, may comprise WF_6. Some possible reactions are shown below in reference to chemical reaction (1) and chemical reaction (2).

$$B_2H_6(g)+WF_6(g)\rightarrow W(s)+2BF_3(g) \quad (1)$$

$$PH_3(g)+WF_6(g)\rightarrow W(s)+PF_3(g) \quad (2)$$

Other by-products include but are not limited to H_2, HF, F_2. Other reactions are also possible, such as decomposition reactions. In other embodiments, other reductants may be used, such as SiH_4. Similarly, in other embodiments, other tungsten containing gases may be used, such as $W(CO)_6$.

The purge gas includes Ar, He, N_2, H_2, other suitable gases, and combinations thereof. One or more purge gas may be used. FIG. **5** is a graphical representation of one embodiment of gases present in a processing chamber utilizing two purge gases Ar and N_2. Each of the processing gases was flowed into processing chamber **37** with a carrier gas, which in this example was one of the purge gases. WF_6 is introduced with Ar and B_2H_6 is introduced with N_2. It should be understood, however, that the purge gas may differ from the carrier gas, discussed more fully below. One cycle of the ALD technique in accordance with the present invention includes flowing the purge gas, N_2, into processing chamber **37** during time t_1, which is approximately about 0.01 to about 15 seconds before B_2H_6 is flowed into processing chamber **37**. During time t_2, the processing gas B_2H_6 is flowed into processing chamber **37** for a time in the range of about 0.01 to about 15 seconds, along with a carrier gas, which in this example is N_2. After about 0.01 to about 15 seconds have lapsed, the flow of B_2H_6 terminates and the flow of N_2 continues during time t_3 for an additional time in the range of about 0.01 to about 15 seconds, purging the processing chamber of B_2H_6. During time t_4 which lasts approximately about 0 to about 30 seconds, processing chamber **37** is pumped so as to remove most, if not all, gases. After pumping of process chamber **37**, the carrier gas Ar is introduced for a time in the range of about 0.01 to about 15 seconds during time t_5, after which time the process gas WF_6 is introduced into processing chamber **37**, along with the carrier gas Ar during time t_6. The time t_6 lasts between about 0.01 to about 15 seconds. The flow of the processing gas WF_6 into processing chamber **37** is terminated approximately about 0.01 to about 15 seconds after it commenced. After the flow of WF_6 into processing chamber **37** terminates, the flow of Ar continues for an additional time in the range of 0.01 to 15 seconds, during time t_7. Thereafter, processing chamber **37** is pumped so as to remove most, if not all, gases therein, during time t_8. As before, time t_8 lasts approximately about 0 to about 30 seconds, thereby concluding one cycle of the sequential deposition technique, in accordance with the present invention. The cycle may be repeated to deposit a tungsten layer to a desired thickness.

The benefits of employing the sequential deposition technique are many fold, including flux-independence of layer formation that provides uniformity of deposition independent of the size of a substrate. For example, the measured difference of the layer uniformity and thickness measured between a 200 mm substrate and a 300 mm substrate deposited in the same chamber is negligible. This is due to the self-limiting characteristics of the sequential deposition techniques. Further, this technique contributes to improved step coverage over complex topography.

In addition, the thickness of the layer B, shown in FIG. **4**, may be easily controlled while minimizing the resistance of the same by employing sequential deposition techniques. With reference to FIG. **6**, it is seen in the slope of line **50** that the thickness of the tungsten layer B is proportional to the number of cycles employed to form the same. The resistivity of the tungsten layer, however, is relatively independent of the thickness of the layer, as shown by the slope of line **52** in FIG. **7**. Thus, employing sequential deposition techniques, the thickness of a refractory metal layer maybe easily controlled as a function of the cycling of the process gases introduced into the processing chamber with a negligible effect on the resistivity.

FIG. **8** is a graphical representation showing the relationship between the deposition rate of a layer formed on a substrate employing sequential deposition techniques and the temperature of the substrate. Control of the deposition rate was found to be dependent upon the temperature of substrate **42**. As shown by the slope of line **54**, increasing the temperature of substrate **42** increased the deposition rate of the tungsten layer B. The graph shows that less than a monolayer, a monolayer, or more than a monolayer of a

tungsten layer may be formed depending on the substrate temperature utilized. For example, at **56**, the deposition rate is shown to be approximately 2 Å/cycle at 250° C. However at point **58** the deposition rate is approximately 5 Å/cycle at a temperate of 450° C. The resistivity of the tungsten layer, however, is virtually independent of the layer thickness, as shown by the slope of curve **59**, shown in FIG. **9**. As a result, the deposition rate of the tungsten layer may be controlled as a function of temperature without compromising the resistivity of the same. However, it may be desirable to reduce the time necessary to deposit an entire layer of a refractory metal.

To that end, a bulk deposition of the refractory metal layer may be included in the deposition process. Typically, the bulk deposition of the refractory metal occurs after the nucleation layer is formed in a common processing chamber. Specifically, in the present example, nucleation of a tungsten layer occurs in chamber **12** employing the sequential deposition techniques discussed above, with substrate **42** being heated in the range of about 200° C. to about 400° C., and processing chamber **37** being pressurized in the range of about 1 to about 10 Torr. A nucleation layer **60** of approximately about 120 to about 200 Å is formed on a patterned substrate **42**, shown in FIG. **10**. Nucleation layers of about 100 Å or less, about 50 Å or less, or about 25 Å or less have also been found to be effective in providing good step coverage over apertures having an aspect ratio of about 6:1 or greater. As shown, substrate **42** includes a barrier layer **61** and a patterned layer having a plurality of vias **63**. The nucleation layer is formed adjacent to the patterned layer covering vias **63**. As shown, forming nucleation layer **60** employing ALD techniques provides good step coverage. In another embodiment, sequential deposition techniques may be performed for both nucleation and bulk deposition. In still another embodiment, to decrease the time required to form a complete layer of tungsten, a bulk deposition of tungsten onto nucleation layer **60** occurs using CVD techniques, while substrate **42** is disposed in the same processing chamber **12**, shown in FIG. **1**. The bulk deposition may be performed using recipes well known in the art. In this manner, a tungsten layer **65** providing a complete plug fill is achieved on the patterned layer with vias having aspect ratios of approximately 6:1, shown in FIG. **11**.

In an alternative embodiment, a bifurcated deposition process may be practiced in which nucleation of the refractory metal layer occurs in a chamber that is different from the chamber in which the remaining portion of the refractory metal layer is formed. Specifically, in the present example, nucleation of a tungsten layer occurs in chamber **12** employing the sequential deposition techniques, such as ALD, discussed above. To that end, substrate **42** is heated in the range of about 200° C. to about 400° C. and chamber **37** is pressurized in the range of about 1 to about 10 Torr. A nucleation layer **60** of approximately 120 to 200 Å is formed on a patterned substrate **42**, shown in FIG. **10**. Nucleation layers of about 100 Å or less, about 50 Å or less, or about 25 Å or less have also been found to be effective in providing good step coverage over apertures having an aspect ratio of about 6:1 or greater. As shown, substrate **42** includes a barrier layer **61** and a patterned layer having a plurality of vias **63**. The nucleation layer is formed adjacent to the patterned layer covering the vias **63**. As shown, forming the nucleation layer **60** employing sequential deposition techniques provides improved step coverage.

In one embodiment, sequential deposition techniques are employed for bulk deposition of tungsten onto nucleation layer **60** occurs while substrate **42** is disposed in processing chamber **14**, shown in FIG. **1**. The bulk deposition maybe performed using recipes disclosed herein. In another embodiment, CVD techniques are employed for bulk deposition of tungsten onto nucleation layer **60** occurs while substrate **42** is disposed in processing chamber **14**, shown in FIG. **1**. The bulk deposition maybe performed using recipes well known in the art. Whether sequential deposition or CVD deposition techniques are employed, a tungsten layer **65** providing a complete plug fill is achieved on the patterned layer with vias having aspect ratios of approximately 6:1, shown in FIG. **11**. Implementing the bifurcated deposition process discussed above may decrease the time required to form a tungsten layer having improved characteristics. Utilizing CVD deposition techniques for bulk deposition may further increase throughput.

As mentioned above, in an alternate embodiment of the present invention, the carrier gas may differ from the purge gas, as shown in FIG. **12**. The purge gas, which is introduced at time intervals t_1, t_3, t_5 and t_7 comprises Ar. The carrier gas, which is introduced at time intervals t_2 and t_6, comprises of N_2. Thus, at time interval t_2 the gases introduced into the processing chamber include a mixture of B_2H_6 and N_2, and a time interval t_6, the gas mixture includes WF_6 and N_2. The pump process during time intervals t_4 and t_8 is identical to the pump process discussed above with respect to FIG. **5**. In yet another embodiment, shown in FIG. **13**, the carrier gas during time intervals t_2 and t_6 comprises H_2, with the purge gas introduced at time intervals t_1, t_3, t_5 and t_7 comprising of Ar. The pump processes at time intervals t_4 and t_8 are as discussed above, As a result, at time interval t_2 the gas mixture introduced into processing chamber **37** comprises of B_2H_6 and H_2, and WF_6, and H_2 at time interval t_6.

An advantage realized by employing the H_2 carrier gas is that the stability of the tungsten layer B may be improved. Specifically, by comparing curve **66** in FIG. **14** with curve **68** in FIG. **15**, it is seen that the concentration of fluorine in the nucleation layer **60**, shown in FIG. **10**, is much less when H_2 is employed as the carrier gas, as compared with use of N_2 or Ar as a carrier gas.

Referring to both FIGS. **14** and **15**, the apex and nadir of curve **66** show that the fluorine concentration reaches levels in excess of 1×10^{21} atoms per cubic centimeter and only as low as just below 1×10^{19} atoms per cubic centimeter. Curve **68**, however, shows that the fluorine concentration is well below 1×10^{21} atoms per cubic centimeter at the apex and well below 1×10^{17} atoms per cubic centimeter at the nadir. Thus, employing H_2 as the carrier gas provides a much more stable film, i.e., the probability of fluorine diffusing into the substrate, or adjacent layer is reduced. This also reduces the resistance of the refractory metal layer by avoiding the formation of a metal fluoride that may result from the increased fluorine concentration. Thus, the stability of the nucleation layer, as well as the resistivity of the same, may be controlled as a function of the carrier gas employed. This is also true when a refractory metal layer is deposited entirely employing ALD techniques, i.e., without using other deposition techniques, such as CVD.

In addition, adsorbing a layer **70**, shown in FIG. **16**, of either PH_3 or B_2H_6 prior to introduction of the tungsten containing compound forms a tungsten layer **72** with reduced fluorine content, improved step coverage, and improved resistivity. This was found to be the case where the tungsten containing compound is introduced over a layer of PH_3 or B_2H_6 employing sequential deposition techniques or employing standard CVD techniques using either tungsten hexafluoride, WF_6, and silane, SiH_4, or tungsten hexafluoride, WF_6, and molecular hydrogen, H_2, chemis-

tries. The improved characteristics of the tungsten film are believed to be attributable to the chemical affinity between the PH_3 or B_2H_6 layer and the WF_6 layer. This provides better surface mobility of the adsorbed chemical species and better reduction of WF_6 at the nucleation stage of the tungsten layer. This has proven beneficial when depositing a tungsten layer adjacent to a titanium containing adhesion layer formed from titanium, Ti, or titanium nitride, TiN. Layer **70** is preferably a monolayer, but in other embodiments may be less than or more than a monolayer. Layer **70** in the film stack, shown in FIG. **16**, shows the formation of the tungsten layer **72**. It is understood that layer **70** may or may not be consumed during formation of the tungsten layer **72**. It is also understood that a plurality of layers **70** and tungsten layers **72** may be deposited to form a tungsten layer to a desired thickness. As shown, layer **70** is deposited on substrate **74** that includes a wafer **76** that may be formed from any material suitable for semiconductor processing, such as silicon. One or more layers, shown as layer **74**, may be present on wafer **76**. Layer **78** may be formed from any suitable material, included dielectric or conductive materials. Layer **78** includes a void **80**, exposing a region **82** of wafer **76**.

FIG. **18** is a detailed cross-sectional view of a substrate in which a titanium-containing adhesion layer is formed between a substrate and a layer of either PH_3 or B_2H_6 during the fabrication of a W layer adjacent to the titanium-containing adhesion layer. The titanium-containing adhesion layer may be formed employing standard CVD techniques. In one embodiment, the titanium-containing adhesion layer is formed employing sequential deposition techniques. To that end, processing gas Aa_x is selected from the group including H_2, B_2H_6, SiH_4 and NH_3. Processing gas Bb_y is a titanium-containing gas selected from the group that includes TDMAT, TDEAT and $TiCl_4$. Also, Ar and N_2 purge gases are preferably employed, although other purge gas may be used.

Referring to FIGS. **2** and **17**, each of the processing gases is flowed into processing chamber **37** with a carrier gas, which in this example, is one of the purge gases. It should be understood, however, that the purge gas may differ from the carrier gas, discussed more fully below. One cycle of the sequential deposition technique, in accordance with the present invention, includes flowing a purge gas into processing chamber **37** during time t_1 before the titanium-containing gas is flowed into processing chamber **37**. During time t_2, the titanium-containing processing gas is flowed into the processing chamber **37**, along with a carrier gas. After t_2 has lapsed, the flow of titanium-containing gas terminates and the flow of the carrier gas continues during time t_3, purging the processing chamber of the titanium-containing processing gas. During time t_4, the processing chamber **37** is pumped so as to remove all gases. After pumping of process chamber **37**, a carrier gas is introduced during time t_5, after which time the reducing process gas is introduced into the processing chamber **37** along with the carrier gas, during time t_6. The flow of the reducing process gas into processing chamber **37** is subsequently terminated. After the flow of reducing process gas into processing chamber **37** terminates, the flow of carrier gas continues, during time t_7. Thereafter, processing chamber **37** is pumped so as to remove all gases therein, during time t_8, thereby concluding one cycle of the sequential deposition technique in accordance with the present invention. The aforementioned cycle is repeated multiple times until titanium-containing layer reaches a desired thickness. For example, in reference to FIG. **18**, after TiN layer **84** reaches a desired thickness, layer **86**, in this example formed from PH_3 or B_2H_6, is deposited adjacent thereto employing sequential deposition techniques, as discussed above. Thereafter, a layer of tungsten **88**, shown in FIG. **18**, is disposed adjacent to layer **86** using the sequential deposition technique or standard CVD techniques, both of which are discussed above. Layer **86** is preferably a monolayer, but in other embodiments may be less than or more than a monolayer. Layer **86** in the film stack, shown in FIG. **18**, shows the formation of the tungsten layer **88**. It is understood that layer **86** may or may not be consumed during formation of the tungsten layer **88**. It is also understood that a plurality of layers **86** and tungsten layers **66** may be deposited to form a tungsten layer to a desired thickness. If desired, a copper layer maybe deposited atop of tungsten layer **88**. In this manner, tungsten may function as a barrier layer.

Referring again to FIG. **2**, the process for depositing the tungsten layer may be controlled using a computer program product that is executed by controller **22**. To that end, controller **22** includes a central processing unit (CPU) **90**, a volatile memory, such as a random access memory (RAM) **92** and permanent storage media, such as a floppy disk drive for use with a floppy diskette, or hard disk drive **94**. The computer program code can be written in any conventional computer readable programming language; for example, 68000 assembly language, C, C++, Pascal, Fortran and the like. Suitable program code is entered into a single file, or multiple files, using a conventional text editor and stored or embodied in a computer-readable medium, such as hard disk drive **94**. If the entered code text is in a high level language, the code is compiled and the resultant compiler code is then linked with an object code of precompiled Windows® library routines. To execute the linked and compiled object code, the system user invokes the object code, causing the CPU **90** to load the code in RAM **92**. The CPU **90** then reads and executes the code to perform the tasks identified in the program.

Although the invention has been described in terms of specific embodiments, one skilled in the art will recognize that various changes to the reaction conditions, i.e., temperature, pressure, film thickness and the like can be substituted and are meant to be included herein. Additionally, while the bifurcated deposition process has been described as occurring in a common system, the bulk deposition may occur in a processing chamber of a mainframe deposition system that is different from the mainframe deposition system in which the processing chamber is located that is employed to deposit the nucleation layer. Finally, other refractory metals may be deposited, in addition to tungsten, and other deposition techniques may be employed in lieu of CVD. For example, physical vapor deposition (PVD) techniques, or a combination of both CVD and PVD techniques may be employed. The scope of the invention should not be based upon the foregoing description. Rather, the scope of the invention should be determined based upon the claims recited herein, including the full scope of equivalents thereof.

What is claimed is:

1. A method of sequential deposition of a tungsten nucleation layer and a bulk tungsten layer over a substrate in a processing chamber, comprising:

introducing a pulse of reducing gas comprising phosphine;

introducing a tungsten containing compound to form the nucleation layer; and:

forming the bulk tungsten layer over the tungsten nucleation layer.

2. A method of depositing a tungsten layer over a substrate in a processing chamber, comprising:

adsorbing a layer over the substrate comprising phosphine; and

introducing a tungsten containing compound to form a tungsten layer, wherein introducing the tungsten containing compound comprises introducing the tungsten containing compound in a sequential deposition technique.

3. A method of forming a tungsten layer over a substrate in a processing chamber, comprising:

presoaking the substrate with phosphine to form a presoak layer over the substrate; and

forming a tungsten layer over the presoak layer by sequentially introducing pulses of a tungsten-containing compound and pulses of a reductant.

4. The method of claim **3**, wherein the substrate is presoaked and the tungsten layer is formed in the same processing chamber.

5. The method of claim **3**, wherein the reductant is selected from the group consisting of hydrogen, silane, diborane and phosphine.

6. The method of claim **3**, further comprising introducing a purge gas at least partially between the pulses of the reductant and the pulses of the tungsten containing compound.

7. The method of claim **3**, wherein the substrate comprises a titanium-containing layer and the presoak layer is formed over the titanium-containing layer.

8. The method of claim **3**, wherein the tungsten layer is a tungsten nucleation layer.

9. The method of claim **8**, further comprising forming a bulk tungsten layer over the tungsten nucleation layer.

10. A method of forming a tungsten layer on a substrate in a processing chamber, comprising:

presoaking the substrate with phosphine to form a presoak layer on the substrate; and

forming the tungsten layer on the presoak layer by an ALD process comprising:

flowing a tungsten-containing compound into the processing chamber;

chemisorbing the tungsten-containing compound to the presoak layer;

purging the processing chamber with a purge gas;

flowing a reductant selected from the group consisting of hydrogen, silane, diborane and phosphine into the processing chamber; and

purging the processing chamber with the purge gas.

11. The method of claim **10**, wherein the substrate is presoaked and the tungsten layer is formed in the same processing chamber.

12. The method of claim **10**, wherein the reductant is diborane.

13. The method of claim **10**, wherein the purge gas is selected from the group consisting of Ar, He, H_2, N_2 and combinations thereof.

14. The method of claim **10**, wherein the substrate comprises a titanium-containing layer and the presoak layer is formed over the titanium-containing layer.

15. The method of claim **10**, wherein the tungsten layer is a tungsten nucleation layer.

16. The method of claim **15**, further comprising forming a bulk tungsten layer over the tungsten nucleation layer.

17. The method of claim **8**, wherein the bulk tungsten layer is deposited by a process selected from the group consisting of ALD, CVD, PVD or combinations thereof.

18. The method of claim **16**, wherein the bulk tungsten layer is deposited by a process selected from the group consisting of ALD, CVD, PVD or combinations thereof.

19. A method of forming a tungsten layer on a substrate in a processing chamber, comprising:

sequentially pulsing a tungsten containing compound and phosphine by an ALD process to deposit a nucleation tungsten layer; and

forming a bulk tungsten layer over the nucleation tungsten layer.

20. The method of claim **19**, wherein the ALD process further comprises a purge gas selected from the group consisting of Ar, He, H_2, N_2 and combinations thereof.

21. The method of claim **20**, wherein the nucleation tungsten layer is deposited on a barrier layer selected from the group consisting of titanium, titanium nitride and combinations thereof.

22. The method of claim **21**, wherein the bulk tungsten layer is deposited by a process selected from the group consisting of ALD, CVD, PVD or combinations thereof.

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